Environment and Climate Change Canada
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Draft Federal Environmental Quality Guidelines

Perfluorooctane Sulfonate (PFOS)

Environment and Climate Change Canada

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Introduction

Federal Environmental Quality Guidelines (FEQGs) provide benchmarks for the quality of the ambient environment. They are based solely on the toxicological effects or hazard of specific substances or groups of substances. FEQGs serve three functions: first, they can be an aid to prevent pollution by providing targets for acceptable environmental quality; second, they can assist in evaluating the significance of concentrations of chemical substances currently found in the environment (monitoring of water, sediment, and biological tissue); and third, they can serve as performance measures of the success of risk management activities. The use of FEQGs is voluntary unless prescribed in permits or other regulatory tools. Thus FEQGs, apply to the ambient environment. They are not effluent limits or "never-to-be-exceeded" values but may be used to derive them. The development of FEQGs is the responsibility of the federal Minister of the Environment under the *Canadian Environmental Protection Act, 1999* (CEPA). The intent is to develop FEQGs as an adjunct to the risk assessment/risk management of priority chemicals identified in the Chemicals Management Plan (CMP) or other federal initiatives. This factsheet provides the Federal Water Quality Guideline (FWQG) (Figure 1), the Federal Fish Tissue Guideline (FFTG) for the protection of aquatic life, the Federal Wildlife Diet Guidelines (FWiDGs) for the protection of mammalian and avian consumers of aquatic biota, and the Federal Tissue Guideline describing the acceptable contaminant levels in bird eggs (FTG-BE) for perfluorooctane sulfonate (PFOS) (Table 1).

FEQGs for water, fish tissue, wildlife diet and bird egg are similar to Canadian Council of Ministers of the Environment (CCME) guidelines in that they are benchmarks for the quality of the ambient environment and are based solely on toxicological effects data. Where data permit, FEQGs are derived following CCME methods. FEQGs differ from Canadian Environmental Quality Guidelines (CEQG) in that FEQGs are developed where there is a federal need for a guideline (e.g. to support federal risk assessment, federal risk management or monitoring activities) but where the CCME guideline(s) for the substance has not yet been developed or is not reasonably expected to be updated in the near future.

This factsheet also provides Federal Soil Quality Guidelines for Agricultural, Residential/Parkland, Commercial and Industrial land uses (Table 2), and Federal Groundwater Quality Guidelines (FGWQG) (Table 3). Whereas the water, fish tissue, diet and groundwater guidelines are designed to protect the ambient environment, the soil FEQGs use the Canadian Council of Ministers of the Environment (CCME) protocol for deriving soil quality guidelines (CCME 2006) to develop guidelines for the assessment and remediation of contaminated sites. The soil FEQGs therefore consider the effects of contaminated soil exposure on ecological receptors and aim to protect remediated soil for specified uses (e.g., agricultural, residential/ parkland, commercial and industrial land use). The soil FEQGs are designed to protect important ecological functions (e.g. direct contact for plants and soil invertebrates, protect against effects in the ecological food chain).

Substance Identity

Perfluorooctane sulfonate (PFOS) belongs to a larger group of fluorochemicals called perfluorinated alkyl compounds (Kissa 1994). This classification indicates that the main carbon chain of the compound is completely saturated with fluorine, involving highly stable C-F bonds. While PFOS can exist in its anionic form ($C_8F_{17}SO_3^-$), it also exists as an acid (CAS No. 1763-23-1), potassium salt (CAS No. 2795-39-3), ammonium salt (CAS No. 29081-56-9), diethanolamine salt (CAS No. 70225-14-8) and lithium salt (CAS No. 29457-72-5). PFOS is not found naturally in the environment, however, it has been manufactured since the 1950s (Lehmler 2005). Based on the Screening Assessment Report (SAR), Environment Canada (EC) (2006) concluded that PFOS, its salts and its precursors (compounds containing the following groups: $C_8F1_7SO_2$, $C_8F1_7SO_3$ or $C_8F1_7SO_2N$) were entering the environment in a quantity that has, or may have, an immediate or long-term harmful effect on the environment and biological diversity. PFOS and its salts and its precursors meet the definition of toxic and PFOS and its salts (but not precursors) are also persistent according to the Persistence and Bioaccumulation Regulations (SOR/2000-107) under CEPA and were added to the Stockholm Convention on Persistent Organic Pollutants Annex B (restricted) in 2009. PFOS is also considered bioaccumulative, despite not strictly meeting the regulatory criteria. Moreover, PFOS and its salts were added to the *Virtual Elimination List* under subsection 65(2) of CEPA with the promulgation of the *Perfluorooctane Sulfonate Virtual Elimination Act*, SOR/2009-15 (Government of Canada 2009).

Table 1. Federal Environmental Quality Guidelines for Perfluorooctane Sulfonate (PFOS) for surface water, fish tissue, wildlife diet, bird egg and sediment*.

Water (µg/L)	Fish Tissue (mg/kg ww)	Wildlife Diet (µg/kg ww food)**		Bird Egg (µg/g ww)
		Mammalian	Avian	
6.8	8.3	4.6	8.2	1.9

* FEQG for soil and groundwater are available in Tables 2 and 3.
**The wildlife diet guidelines are intended to protect either mammalian or avian species that consume aquatic biota. It is the concentration of PFOS in the aquatic biota food item, expressed on whole body, wet weight basis that could be eaten by terrestrial or semi-aquatic mammalian or avian wildlife.

Table 2. Federal Soil Quality Guidelines for Perfluorooctane Sulfonate (PFOS). See footnotes for explanation.

Pathway	Agricultural	Residential/ Parkland	Commercial	Industrial
Final Proposed Federal Soil Quality Guideline (FSQG)	**0.01 mg/kg**	**0.01 mg/kg**	**0.14 mg/kg (coarse soil)[1] 0.21 mg/kg (fine soil)[2]**	**0.14 mg/kg (coarse soil)[1] 0.21 mg/kg (fine soil)[2]**
Soil Contact ($FSQG_{SC}$)	11 mg/kg	11 mg/kg	61 mg/kg	61 mg/kg
Soil Ingestion ($FSQG_{1C}$)	2.2 mg/kg soil	2.2 mg/kg soil	NR	NR
Soil Ingestion ($FSQGC_{2C}$)	0.01 mg/kg soil	0.01 mg/kg soil	NR	NR
Soil Ingestion ($FSQG_{3C}$)	0.6 mg/kg soil	0.6 mg/kg soil	NR	NR
Agricultural (Livestock watering- $FSQG_{LW}$)	12 mg/kg coarse soil 9 mg/kg fine soil	NR	NR	NR
Soil Quality Guideline to Protect Freshwater Life ($FSQG_{FL}$)[3]	0.14 mg/kg (coarse soil) 0.21 mg/kg (fine soil)			
Check Mechanisms				
Nutrient and Energy Cycling	NC	NC	NC	NC
Offsite migration ($FSQG_{OM-E}$)[4]	NR	NR	0.14 mg/kg	0.14 mg/kg

Notes:

NC = Not calculated
NR = Not required
1C = Primary consumer, 2C = Secondary consumer, 3C = Tertiary consumer; FL = Freshwater life; LW = Livestock watering; OM-E = Off-site migration- environmental.
[1] Coarse-grained soil is soil which contains more than 50% by mass particles larger than 75 µm mean diameter (D50 > 75 µm).
[2] Fine-grained soils are soils which contain more than 50% by mass particles smaller than 75 µm mean diameter (D50 < 75 µm).
[3] $FSQG_{FL}$ is the concentration in soil that is expected to protect against potential impacts on freshwater aquatic life from PFOS originating in soil that may enter the groundwater and subsequently discharge to a surface water body. This pathway is applicable under any land use category, where a surface water body sustaining aquatic life is present (i.e., within 10 kilometres of the site). Where the distance to the nearest surface water body is greater than 10 kilometres, application of the pathway should be evaluated on a case-by-case basis by considering the site-specific conditions.[4] Soil quality guidelines for commercial and industrial sites consider receptors exposed to on-site soil. However, wind and water erosion of soil and subsequent deposition can transfer contaminated soil from one site to another. The $FSQG_{OM-E}$ pathway addresses the movement of soil from a commercial or industrial site to an adjacent, more sensitive site (e.g. agricultural property). Given the uncertainties surrounding the model used to generate the $FSQG_{OM-E}$, it is considered to be a check mechanism and professional judgement should be used to determine whether the soil quality guideline should be modified by this pathway (CCME 2006).

Table 3. Federal Groundwater Quality Guidelines for Perfluorooctane Sulfonate (PFOS) Considering Ecological Receptors.

	Soil Type	
	Coarse[2]	Fine[3]
Federal Groundwater Quality Guideline - Final ($FGWQG_{Final}$)[1]	**0.068 mg/L**	**0.068 mg/L**
Groundwater Contact ($FGWQG_{GC}$) by soil-dependent organisms	2 mg/L	2 mg/L
Protection of freshwater life ($FGWQG_{FL}$)[4]	0.068 mg/L	0.068 mg/L
Protection of marine life ($FGWQG_{ML}$)	NC	NC
Protection of livestock watering ($FGWQG_{LW}$)	NC	NC
Protection of irrigation water ($FGWQG_{IR}$)	NC	NC
Management considerations ($FGWQG_{M}$)- solubility	370 mg/L	370 mg/L

Notes: [1] The federal groundwater quality guideline-final ($FGWQG_{Final}$) is the lowest of the pathway–specific guidelines while also taking the solubility of the substance into account.
2 Coarse-grained soil is soil which contains more than 50% by mass particles larger than 75 µm mean diameter (D50 > 75 µm).
3 Fine-grained soils are soils which contain more than 50% by mass particles smaller than 75 µm mean diameter (D50 < 75 µm).
[4] $FGWQG_{FL}$ is the concentration in groundwater that is expected to protect against potential impacts on freshwater life from PFOS originating in soil that may enter groundwater and subsequently discharge to a surface water body. This pathway may be applicable under any land use category, where a surface water body sustaining aquatic life is present (i.e., within 10 kilometres of the site). Where the distance to the nearest surface water body is greater than 10 kilometres, application of the pathway should be evaluated on a case-by-case basis by considering the site-specific conditions.
NC = not calculated.

Uses

Between 1997 and 2000, Canada imported approximately 600 tonnes of perfluorinated alkyl compounds. PFOS and its precursors, (the precursors contribute to overall loading in the environment), accounted for 43% of these compounds, while PFOS alone accounted for <2% (EC 2001). PFOS and PFOS-related compounds are used as water, oil, soil and grease repellents. Their use can be categorized into three main categories: surface treatment of apparel and home furnishings, paper protection, and performance chemicals. In the past, PFOS surface treatments were used in industrial manufacturing, in such settings as textile mills, leather tanneries, fibre production lines and carpet manufacturing plants (OECD 2002). Food and non-food industries used PFOS and PFOS-related chemicals in paper applications including food containers, food wrappers, folding cartons and masking papers (OECD 2002, Dallaire et al. 2009; Château-Degat et al. 2010; Clarke et al. 2010). Specifically, the potassium salt of PFOS, used in the manufacture of aqueous film forming foams (AFFFs), was the most significant perfluorinated alkyl compound imported into Canada (EC 2013a). As performance chemicals, PFOS-related chemicals were used in a variety of ways, for example, mining and oil well surfactants, photographic film, hydraulic fuel additives, electronics chemicals, denture cleaners and shampoos. Salts of PFOS were also used specifically as acid mist suppressants for metal plating and electronic etching baths, floor polishes, alkaline cleaners, insecticide in bait stations and as fire-fighting foams (3M Company 2000). By 2002, the primary producer in the United States completed phase out the production of PFOS chemicals and products containing PFOS. However, China began large-scale PFOS production in 2003 (Butt et al., 2010); in 2006 they produced more than 200 tons of the precursor, perfluorooctanesulfonyl fluoride (POSF) (Ministry of Environmental Protection of China 2008).

The manufacture, importation and use of PFOS and PFOS related compounds in Canada is regulated under the *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulation*, SOR/2008-178 (Government of Canada 2008) pursuant to the *Canadian Environmental Protection Act (CEPA)*. This regulation prohibits the manufacture, import, sale, offer for sale and use of PFOS or of products containing PFOS, unless incidentally present, with certain exemptions (*e.g.*, AFFF), aviation hydraulic fluids under certain conditions, and some products used in photographic or photolithographic process) (Government of Canada 2008).

Measured concentrations

Concentrations of PFOS have been measured in various environmental media including water, fish, wildlife, sediment, air and soil. Early studies on PFOS detected concentrations in the environment ranging from a few pg/m^3 in air (Kim and Kannan 2007) to high µg/kg levels in wildlife (Giesy and Kannan 2001, 2002; Kannan et al. 2001a,b, 2002a,b, 2005; Tao et al. 2006). PFOS is the most commonly found perfluorinated compound (PFC) in the tissues of wildlife, accumulating primarily in the blood and liver (Giesy and Kannan 2001). Kannan et al. (2006) reported that PFC concentrations in polar bears were the highest in any species to date. Maximum levels of PFOS in liver of Canadian Arctic biota have been reported for mink (20 µg/kg), seal (37 µg/kg), brook trout (50 µg/kg), fox (1400 µg/kg) (Martin et al. 2004) and polar bear (3770 µg/kg) (Smithwick et al. 2005).

Most recently, the CMP monitoring program reported PFOS concentrations from locations across Canada over the period 2006-2011 in various media (Environment and Climate Change Canada (ECCC) 2016, Government of Canada 2016, EC 2013b). Between 2007 and 2010, Environment Canada collected water samples (n = 569) from 11 drainage regions across Canada (Pacific Coast, Fraser-Lower Mainland, Okanagan-Similkameen, Yukon, Assiniboine-Red, Great Lakes, Ottawa, St. Lawrence, St. John-St. Croix, Maritime Coastal and Newfoundland-Labrador). All surface water samples had PFOS concentrations at least 200-fold lower than the FEQG for water (6.8µg/L). The maximum surface water concentration reported was 10 ng/L (0.01µg/L).

In the 2011-2014 CMP monitoring period, PFOS concentrations were below the FEQG for fish health in all 11 drainage regions sampled (Government of Canada 2016). Importantly however, in some instances, PFOS levels in fish exceeded the FEQG for the protection on mammals and birds that eat the fish, suggesting that this compound could represent a potential risk to wildlife predators in 7 of 11 drainage regions (Columbia, Yukon, Assiniboine-Red, Winnipeg, Great Lakes, St. Lawrence and Maritime Coastal). In the analysis of concentrations of PFOS in lake trout from Lake Ontario from 1979-2014, geometric mean lake trout tissue concentrations rose from 1979-2002, peaking at approximately 80 to 110 µg/kg wet weight in 2002 and then appear to be decreasing to approximately 40-60 µg/kg by 2013-2014 (ECCC 2016).

Similarly in 2006 and 2010, Environment Canada collected top predator fish (lake trout and walleye) (n = 441) from 21 sites in 13 drainage regions and analyzed PFOS in their tissue (Government of Canada 2016, EC 2013b). PFOS levels varied considerably with the highest concentrations in urban areas compared with more remote lakes. The highest concentrations in lake trout were from Lake Erie (geometric mean = 90 µg/kg ww) and Lake Ontario (geometric mean = 62 µg/kg ww) and mostly low (< 3 µg/kg ww) in fish from water bodies located in northern Canada, Pacific and Atlantic regions and Lake Superior. Notably, the analysis found that the concentration of PFOS was below the FEQG for fish health (i.e. below 8.3 mg/kg ww = 8300 µg/kg ww) in all sampled drainage regions (Pacific Coast, Okanagan-Similkameen, Columbia, Yukon, Peace-Athabasca, Lower Mackenzie, Assiniboine-Red, Winnipeg, Lower Saskatchewan-Nelson, Churchill, Great Lakes, St. Lawrence, and Maritime Coastal). As in the more recent studies however, PFOS levels in fish exceeded the FEQG for the protection on mammals and birds that eat the fish, suggesting that this compound could represent a potential risk to wildlife predators. At that time, eight of the 13 sampled drainage regions (Okanagan-Similkameen, Columbia, Assiniboine-Red, Winnipeg, Lower Saskatchewan, Great Lakes, St. Lawrence and Maritime Coastal) had some concentrations of PFOS that exceeded the FEQG for wildlife (i.e. 4.6 µg/kg ww food for mammals, and 8.2 µg/kg ww food for birds).

CMP also monitored PFOS in gull and starling eggs from 2008-2011to characterize PFOS in aquatic and terrestrial birds, respectively (EC 2013b). In individual gull eggs, PFOS concentrations were relatively elevated in the Great Lakes and St. Lawrence River with levels > 0.260 µg/g ww. Concentrations were lower (0.007 to 0.115 µg/g ww) in non-urban areas as well as in marine colonies on both the Atlantic and Pacific coasts. Pooled samples collected between 2009 and 2011 similarly showed the highest concentration in gull eggs were from Lake Erie (0.676 µg/g ww). Starlings are terrestrial birds and feed lower on the food web than gulls; and while the highest concentrations of PFOS in starling eggs were those located at the Brantford, Ontario landfill (0.702 µg/g ww) which is located in a highly urbanized region in southern Ontario, concentrations in urban sites and landfill sites generally overlapped. Concentrations of PFOS in starling eggs at urban sites were: Indus, Alta (0.199 µg/g ww), Delta B.C. (0.075 µg/g ww), Hamilton, Ont. (0.041 µg/g ww) compared with starlings eggs at landfill sites located in Halton, Ont (0.029 µg/g ww), Stoney Creek, Ont. (0.028 µg/g ww) and Otter Lake, NS (0.018 µg/g ww), and Langley, B.C. (0.0056 µg/g ww). In all cases the levels in eggs of terrestrial and aquatic-feeding birds were below the FEQG for bird egg (1.9 µg/g ww).

In 2008, 65 surface sediment samples were collected at 18 sites across Canada (EC 2013b). The highest PFOS concentration in sediment was found in Lake Ontario (0.010 µg/g dry-weight). Values were also reported to range from 0.00016 to 0.0024 µg/g dry weight for sediments in Lake Erie, Lake Huron, Lake Superior, Hamilton harbour, Toronto harbour, near Thunder Bay, Lake Saint Pierre, Nappan River (NB), Kejimikujik Lake (NS), Little Sackville (NS) and Osoyoos Lake (B.C.). PFOS was non-detectable at the other sites monitored.
Average PFOS concentrations in suspended sediments from the Niagara River at Niagara-on-the-Lake, collected annually over a 22 year period (1980-2002) increased from < 0.0004 µg/g (<400 pg/g)in the early 1980s to more than 0.001 µg/g (1000 pg/g) in 2002 (Lucacui et al. 2005). FEQGs for PFOS do not exist for sediment.

Monitoring PFOS in air across Canada provides information on PFOS levels within the country as well as quantities entering Canada from international sources (EC 2013b). Air measurements have been obtained using two methods: high volume air sampling and passive air sampling. High volume air samplers measure a larger volume of air and are better for detecting the low PFOS concentrations often found in the environment. However, passive air samplers can be advantageous under many circumstances because of their simplicity, ease of transport to remote sites, and because they do not require a power source. Sampling using high-volume samples was conducted at three locations in Canada in 2009 (EC 2013b), and it was observed that PFOS concentrations (geometric mean) were more three times higher in Toronto (1.5 pg/m^3) compared with Lake Superior air (0.43 pg/m^3). PFOS was below the detection limit of 0.2 pg/m^3 at the Canadian High Arctic station of Alert, Nun; however its precursors were detected up to several pg/m^3.

Sampling using passive samplers was conducted at eight locations across Canada over a three-month period in 2009 (EC 2013b). PFOS concentrations were detected in Toronto, ON (8 pg/m^3), an agricultural site in Saskatchewan (5 pg/m^3), Whistler, BC (4 pg/m^3), and Alert, NU (2 pg/m^3). One site in northern Ontario had elevated PFOS concentration of 18 pg/m^3. However these data points were only based on one sample. PFOS was not detected at the other Canadian sites. The PFOS levels measured in Canada using passive samplers were substantially lower than in Paris, France (150 pg/m^3), but comparable to Sydney, Florida (3.4 pg/m^3), Tudor Hill, Bermuda (6.1 pg/m^3), Malin Head, Ireland (3.3 pg/m^3), and Hilo, Hawaii (6.6 pg/m^3)[3].

In general, the results showed that PFOS air concentrations in urban locations (e.g., Toronto) were on the same order of magnitude as more remote sites (e.g., Lake Superior), demonstrating the widespread distribution of PFOS in the Canadian atmosphere. FEQGs do not exist for PFOS in air. PFOS precursors measured in the air of Toronto identified average concentrations of N-MeFOSE alcohol of 101 pg/m^3 and N-EtFOSE alcohol (see list of abbreviations below) of 205 pg/m^3 (Martin et al. 2002). Boulanger et al. (2004) reported mean surface water (4 m depth) concentrations of 31 (sd = 6.9) ng/L for Lake Erie and 54 (sd = 18) ng/L for Lake Ontario.

PFOS has been detected in groundwater collected from commercial and industrial sites where AFFFs have been used in firefighting training exercises, or where spills have resulted in either contamination or suspected contamination of soil, surface water and/or groundwater. PFOS concentrations in groundwater at London International Airport (ON), were found to range from <5 to 130 µg/L at a former firefighting training area (Lebel 2012). In an investigation of a firefighting training site at Hamilton International Airport, PFOS concentrations in groundwater ranged from <0.02 to 560 µg/L (exp. Services Inc 2011).

Canadian data regarding background (ambient) PFOS levels in soils were not located (Sanexen 2015). PFAs associated with suspected AFFF-impacted areas have been identified (exp. Services Inc 2011; OAG 2012). OAG (2012) confirmed the presence of PFOS in at 18 Canadian airports (Prince George, BC; Victoria, BC; Campbell River, BC; Williams Lake, BC; Abbotsford, BC; Sandspit, BC; Cambridge Bay, NU; Winnipeg, MB; Watson Lake, YT; London, ON; Ottawa, ON; Thunder Bay, ON; Sault Ste Marie, ON; Hamilton, ON; Fredericton, NB; Halifax, NS; St John's NL; Inuvik, NT). However, at that time the OAG 2012 report stated it was difficult to accurately quantify concentrations of PFOS in soil and groundwater. At the former fire training facility at Hamilton International Airport, PFOS concentrations in soils ranged from <0.025 to 26 mg/kg (exp. Services Inc. 2011).

Fate, behaviour and partitioning

Understanding of the environmental fate of PFOS continues to improve with advances both in experimental data and predictive approaches, although the compounds' physical/chemical properties, notably its hydrophobic/oleophobic nature, continue to make this challenging (Rayne and Forest 2009a, Jing et al. 2009). Due to the high surface-active (surfactant) properties octanol/water (K_{ow}) partition coefficient cannot be measured simply (OECD 2002), although an indirect measure using ion-transfer cyclic voltammetry has determined a log P of 2.45 indicating lipophilicity (Jing et al. 2009). Also sediment organic carbon – water partition coefficients (K_{oc}) for PFCs (Rayne and Forest 2009b) indicate that although longer unbranched sulfonates and carboxylates tended to partition to organic matter, there was high variability in partitioning on a congener- and isomer-specific basis. PFOS is persistent in the environment and the strength of the carbon-fluorine bond renders it resistant to hydrolysis, photolysis and biodegradation. It is therefore considered to be an environmentally stable compound (EC 2006). PFOS appears to be the end stage metabolite or ultimate degradation product of several fluorochemicals produced using perfluorooctane sulphonyl fluoride (Giesy and Kannan 2002). Thus, PFOS precursors contribute to the overall loading of PFOS in the environment.

PFOS is expected to behave differently than traditional hydrophobic pollutants, as it contains both hydrophobic and hydrophilic functional groups. The potassium salt of PFOS has a solubility of approximately 680 mg/L in pure water, 370 mg/L in fresh water, and 12.4 mg/L in sea water (OECD 2002). As a strong acid, PFOS will completely dissociate to ionic forms in neutral water (Jones et al. 2003). In addition, PFOS is not expected to volatilize based on its vapour pressure and predicted Henry's Law constant (OECD 2002). A number of studies report significant sorption of PFOS to sediments (Higgins and Luthy 2006; Nakata et al. 2006) while others do not (Hansen et al. 2002; Senthilkumar et al. 2007). It has therefore been suggested that the sorption and desorption behaviour of PFOS may be greatly affected by different sorption conditions, such as the physiochemical characteristics of the sorbent and the environmental conditions of the aqueous system (Liu et al. 2001). You et al. (2010) inferred that PFOS would be largely removed from the water column with an increase in salinity or pH, and get trapped in the sediments with little bioavailability. In addition, these researchers found correlations between distribution coefficients (K_d) and the fraction of organic carbon, demonstrating that despite its surfactant properties hydrophobic partitioning is important to the sorption of PFOS to soil and sediments.

Bioconcentration factors (BCF – water exposures only) for PFOS ranged from 31.6 to 3614 L/kg for whole body measurements, with an average value of 779 L/kg. The highest value came from a laboratory study performed on bluegill sunfish (*Lepomis macrochirus*) (Drottar et al. 2002). BCFs ranged from 484 to 5400 L/kg in specific tissues, with an average value of 2660 L/kg. The maximum value of 5400 L/kg was calculated for rainbow trout (*Oncorhynchus mykiss*) liver (Martin et al. 2003). Bioaccumulation factors (BAF water and dietary exposure, or field measured) for whole body ranged from 113 to 11 150 L/kg and the maximum value of 11 150 L/kg was observed in brown mussel (*Perna perna*) (Quinete et al. 2009). Tissue-specific BAFs (liver) ranged from 460 to 275 000 L/kg; the highest value was for livers of tucuxi dolphin (*Sotalia guianensis*) (Quinete et al. 2009). Based on data presented in SAR (EC 2006), a geometric mean BAF value of 1614 L/kg was derived for aquatic organisms. The value was based on data for six fish and four invertebrate species. For freshwater organisms, whole body biomagnification factors (BMF) ranged from 0.17 to 7.5 with the mean value of 2.6. The maximum BMF of 7.5 was observed by Houde et al. (2008) and represents the trophic transfer from an invertebrate (*Diporeia hoyi*) to the forage fish, slimy sculpin (*Cottus cognatus*). EC (2006) therefore concluded that PFOS is bioaccumulative even though its surfactant properties resulted in it not meeting the strict definition in the *Persistence and Bioaccumulation Regulations* (SOR/2000-107).

BCFs for PFOS in 16 terrestrial plants species (dry weight basis) ranged from 0.003 to 1.6, with a geometric mean value of 0.35. The highest value came from a study of ryegrass (Brignole et al. 2003). BCFs (dry weight basis) in the terrestrial invertebrate, *Eisenia fetida*, ranged from 2.6 to 34.2, with a geometric mean value of 10.9 (Stubberud 2006). Biomagnification in a lichen-caribou-wolf food web indicated biomagnification was tissue specific ranging from a low of 0.8 for wolf $_{liver}$/caribou $_{liver}$ to a high of 9.1 caribou $_{whole}$/vegetation (Müller et al 2011). For the two caribou herds studied, the mean BMF from soil to caribou was 2.97. Small sample size studies with sheep (Kowaleczyk et al. 2012) and cows (Vestegren et al. 2013) also indicate bioaccumulation of PFOS from diet (food and water). Bioconcentration and bioaccumulation studies indicate that FEQGs for soil for agricultural and residential/parkland uses should consider not only direct soil contact exposure to plants and invertebrates, but also exposure to primary, secondary and tertiary-level food web organisms.

Mode of Action

While the modes of action of PFOS are not entirely understood, they certainly seem diverse. Suggested modes of action include activation of the nuclear peroxisome proliferator activated receptor-alpha (PPAR-α) (Berthiaume and Wallace 2002; Hickey et al 2009, Rosen et al. 2010). These receptors alter gene expression related to a broad spectrum of action but include fatty acid metabolism and transport, cholesterol transport (Feige et al. 2006), glucose metabolism, inflammation response and development. In contrast, toxic effects have been demonstrated that do not involve PPAR mechanisms (O'Brien et al. 2009). PFOS is also believed to interfere at the mitochondrial level through the uncoupling of oxidative phosphorylation. This uncoupling causes a reduction in the production of ATP, thereby reducing energy stores. Other modes of action that have been hypothesized include inflammation-independent leakage of liver cell membranes in fish, which leads to cell necrosis (Hoff et al. 2003); an interference with the homeostasis of DNA metabolism (Hoff et al. 2003); inhibition of glycogen synthesis; increased glycogen breakdown (Hagenaars et al. 2008); and, the inhibition of intercellular communication processes involving gap junctions (Hu et al. 2002). Altered neurochemistry from a single dose of PFOS to neonatal mice resulted in developmental neurotoxicity (Johansson et al. 2008). Finally, endocrine modulation effects on the estrogen receptor and thyroid receptor occurred in zebrafish (Du et al. 2013).

Aquatic Toxicity

Aquatic toxicity values for chronic (long-term) exposures to PFOS (87-99% active ingredient) ranged from 10 to 53000 µg/L, with sensitivities overlapping among taxa (Table 4). At 10 µg/L there were no effects on damselfly survival during a 320-d exposure whereas medaka showed reduced growth in a 14-d exposure (Table 4). Plant data were the most diverse. The most sensitive plant species was watermilfoil (*Myriophyllum sibiricum*) with a 42-d EC_{10} for reduced growth of 100 µg/L. Data were found for two amphibians; there were no effects on survival of African clawed frog (*Xenopus laevis*) at 100 ug/L whereas the 60-d maximum acceptable toxicant concentration for development in leopard frog (*Rana pipiens*) was 1732 µg/L. The 21-day LC_{10} for survival of early life stage of rainbow trout (*Oncorhynchus mykiss)* was 470 µg/L (EC 2014).

Wildlife Toxicity

PFOS is hepatotoxic and the effects include increased liver weights, observed in mallards, northern bobwhite and laboratory rats (Gallagher et al. 2003a; Luebker et al. 2005; York 1999), as well as hepatocellular adenomas (EC 2006) and peroxisome proliferation (Luebker et al. 2005). McNabb et al. (2005) studied the effects of PFOS on the thyroid function in northern bobwhite. After seven days of exposure to a dose of 5 mg/kg body weight (bw), plasma thyroid hormones decreased, indicating organism-level hypothyroidism. When cynomolgus monkeys were administered PFOS (0.03, 0.15, 0.75 mg/kg bw.day for 26 weeks), they had reduced high density lipoprotein and cholesterol (Thomford 2000). Other previously-observed toxic effects of PFOS have included a reduction in testicular size and altered spermatogenesis in both quails and mallards, reduced survival of quail chicks exposed only *in ovo* (Gallagher et al. 2003a,b; Newsted et al. 2007), and a reduced dam body mass in rats (York 1999). Thresholds for effects are similar in mammals and birds (Newsted et al. 2007).

Terrestrial Toxicity

Terrestrial toxicity values for direct soil exposure to 8 plant species (alfalfa (*Medicago sativa*), ryegrass (*Lolium perenne*), soybean (*Glycine max*), lettuce (*Lactuca sativa*), flax (*Linum usitatissimum*), tomato (*Lycopersicon esculentum*), onion (*Allium cepa*) and pak choi (*Brassica chinensis)* (Brignole et al. 2003, Zhao et al. 2011)) and 3 invertebrate species, *Eisenia fetida*, *Folsomia candida* and *Oppia nitens* (Stubberud 2006, Joung et al. 2010 and EC 2015a) to PFOS ranged from 3.9 to 1000 mg/kg soil, with sensitivities overlapping between plants and invertebrates. At 3.9 mg/kg there was 23% reduction in height in lettuce (*Latuca sativa*) during 21-d exposure whereas soybean (*Glycine max*) showed no effect on emergence or mortality at 1000 mg/kg with a 21-d exposure (Brignole et al. 2003). EC_{25} and IC_{25} data were found for 7 plant species and 3 invertebrate species ranging from 3.9 to 393 mg/kg (Table 5).

Federal Environmental Quality Guidelines Derivation

Federal Water Quality Guidelines

The Federal Water Quality Guideline (FWQG) developed here identifies a benchmark for aquatic ecosystems that are intended to protect all forms of aquatic life for indefinite exposure periods. A species sensitivity distribution (SSD) curve was developed using the long-term toxicity data for two amphibian, five fish, five invertebrate and eight plant species (Figure 1 and Table 4). Each species for which appropriate toxicity data were available was ranked according to sensitivity, and its position on the SSD was determined. This guideline is only applicable to freshwater aquatic life first, because there were no marine data, and second, because PFOS is expected to behave differently due to reduced solubility in marine water, as discussed. Fish tissue guidelines or wildlife dietary guidelines (see below) should be used in conjunction with water quality guidelines where a substance may bioaccumulate in higher trophic levels.

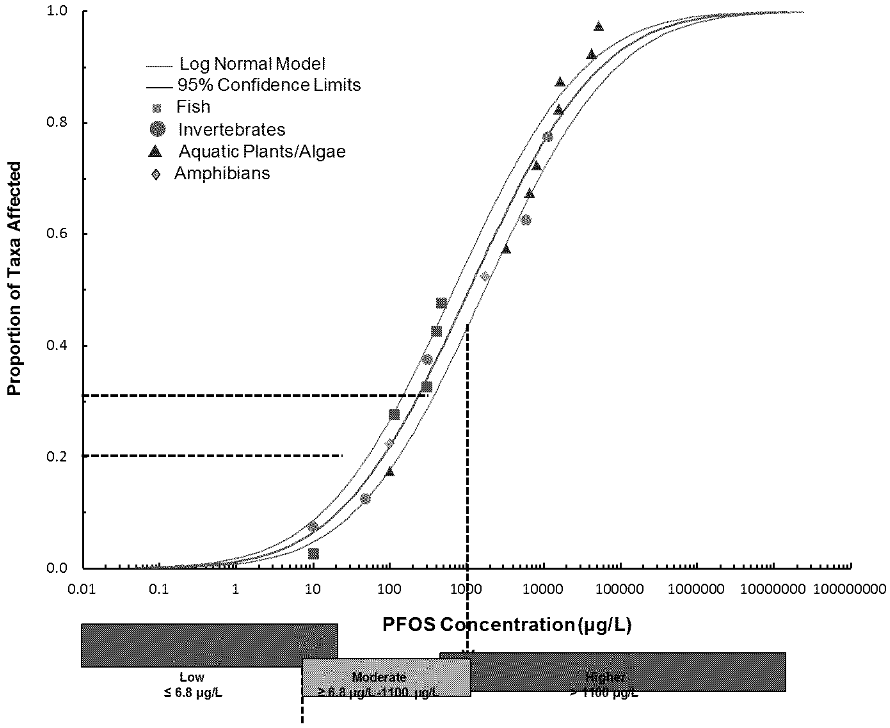

Figure 1.Species sensitivity distribution (SSD) for the chronic toxicity of PFOS and relative likelihood of adverse effects of PFOS to freshwater aquatic life.

The Canadian Water Quality Guideline protocol (CCME 2007) was followed for developing the FWQG for PFOS, with the exception that three surrogate species were included. Several cumulative distribution functions were fit to the data using regression methods and the best model was selected based on goodness-of-fit. The log normal model provided the best fit for these data and the 5th percentile of the SSD plot is 6.8 µg/L, with lower and upper confidence limits of 4.2 and 11 µg/L, respectively (Figure 1).

Table 4. Chronic Aquatic Toxicity Data Used for Developing the Federal Water Quality Guideline for PFOS. (abbreviations for endpoints appended following the reference section).

Species	Group	Endpoint	Concentration (µg/L)	Reference
Japanese medaka (*Oryzias latipes*)		14-d LOEC (growth)	10	Ji et al. (2008)
Damselfly (*Enallagma cyathigerum*)		320-d NOEC (survival)	10	Bots (2010)
Aquatic midge (*Chironomus tentans*)		10-d NOEC (growth, survival)	49	MacDonald et al. (2004)

Watermilfoil (*Myriophyllum sibiricum*)	▲	42-d EC_{10} (growth)	100	Hanson et al. (2005)
African clawed frog (*Xenopus laevis*)	◇	67-day NOEC (survival)	100	Cheng et al. (2011)
Zebrafish (*Danio rerio*)	■	40-d MATC (growth)	112	Du et al. (2009)
Bluegill sunfish (*Lepomis macrochirus*)	■	35-d MATC (survival)	300	Drottar et al. (2002)
Water flea (*Moina macrocopa*)	●	7-d LOEC (reproduction)	313	Ji et al. (2008)
Fathead minnow (*Pimephales promelas*)	■	42-d MATC (survival)	400	Drottar and Krueger (2000a)
Rainbow trout (*Oncorhynchus mykiss*)	■	21-d LC_{10} (survival)	470	EC (2014)
Leopard frog (*Rana pipiens*)	◇	60-d MATC (development)	1732	Ankley et al. (2004)
Watermilfoil (*Myriophyllum spicatum*)	▲	28-d EC_{10} (dry weight)	3300	Hanson et al. (2005)
Water flea (*Daphnia pulicaria*)	●	21-d EC_{10} (survival)	6000	Sanderson et al. (2004)
Duckweed (*Lemna gibba*)	▲	7-d IC_{10} (wet weight)	6600	Boudreau et al. (2003)
Green algae (*Chlorella vulgaris*)	▲	96-h IC_{10} (cell density)	8200	Boudreau et al. (2003)
Water flea (*Daphnia magna*)	●	21-d EC_{10} (survival)[a]	12000	Boudreau et al. (2003) Sanderson et al. (2004)
Green algae (*Selenastrum capricornutum*) (also known as *Pseudokirchneriella subcapitata*)	▲	96-h IC_{10} (cell density)[a]	16000	Boudreau et al. (2003) Drottar and Krueger (2000b)
Diatom (*Navicula pelliculosa*)	▲	96-h MATC (growth)	16500	Sutherland and Krueger (2001)
Blue-green algae (*Anabaena flos-aquae*)	▲	96-h IC_{10} (cell density)	42600	Desjardins et al. (2001)
Green algae (*Scenedesmus obliquus*)	▲	72-h IC_{10} (growth)[a]	53000	Liu et al. (2008)

Legend: ◇ =Amphibian; ■ = Fish; ● = Invertebrate; ▲ = Plant
[a] Effect concentration is the geometric mean of comparable endpoints

The 5th percentile of 6.8 µg/L, calculated from the SSD, is the Federal Water Quality Guideline for protection of freshwater organisms (Figure 1). No uncertainty factor was used here because the SSD is comprised mostly of "no effect" data (CCME 2007).The guideline represents the concentration at which one would expect only a very low likelihood of adverse effects on aquatic life. In addition to this guideline, two additional concentration ranges are provided for use in risk management. At concentrations between greater than the FWQG and the 50th percentile of the SSD (i.e. >6.8 to 1100 µg/L) there is a moderate likelihood of adverse effects to aquatic life. Concentrations greater than the 50th percentile (> 1100 µg/L) have a higher likelihood of adverse effects. The "moderate" and "higher" benchmarks may be used in setting less protective interim targets for waters that are already degraded or where there may be socio-economic considerations that preclude the ability to meet the FWQG. This value is not designed to protect against possible bioaccumulation exposures of higher trophic levels. Instead, tissue residue concentrations are developed below.

Federal Fish Tissue Guideline

The Federal Fish Tissue Guideline (FFTG) is a benchmark for aquatic ecosystems that is intended to protect fish from the direct adverse effects of bioaccumulated contaminants. FFTGs supplement water quality guidelines in that they provide a different metric with which to assess potential adverse effects. FFTGs apply to both freshwater and marine fish, and specify the concentration of PFOS found in whole body fish tissue (wet weight) not expected to

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result in adverse effects to the fish themselves. The FFTG may not be appropriate to evaluate the impacts of PFOS found in other aquatic biota (amphibians, invertebrates or plants).

It is preferable to develop tissue guidelines from studies that relate tissue concentrations to toxic effects. A study with bluegill, designed to measure bioaccumulation also provided information on residues related to toxic effects (Drottar et al. 2002). Bluegill exposed to 0.086 mg/L PFOS for 62 days accumulated 81 mg/kg ww without significant effects on survival. In contrast, bluegill exposed to 0.87 mg/L experienced heavy mortality at tissue residues starting at 159±16 mg/kg ww ranging to 241±29 mg/kg ww on day 28, at which point mortality was nearly complete. Dividing the no effect value by a safety factor of 10 gives a FFTG of 8.1 mg/kg whole body wet weight.

This value is corroborated by using an equilibrium partitioning approach to estimate a whole body concentration from the federal water quality guideline and the degree to which fish accumulate PFOS either directly from water (bioconcentration factors) or via both food and water (bioaccumulation factors) Although PFOS accumulates in the liver, and is hepatotoxic, monitoring efforts have been directed at measuring the concentration of PFOS in the whole body of fish. Therefore, although liver BAF values were available for PFOS, the FFTG developed here is based on the whole-body accumulation of PFOS.

Accumulation factors, summarized in EC 2006, included lab and field studies with fish, invertebrates and algae from marine and fresh waters, and were reported on a wet-weight (ww) basis. The geometric mean values selected for the calculation were BCFs for bluegill sunfish (Drottar et al. 2002) and carp (Inoue et al 2012). BCF/BAF values for marine fish were generally higher, but were not considered.

The FFTG was developed as follows:

$$\text{FFTG} = (\text{FWQG})\ (\text{BAF}_{geomean}) = (6.0\ \mu\text{g/L})\ (1378\ \text{L/kg}) = 8.3\ \text{mg/kg ww}$$

Therefore the FFTG is 8.3 mg/kg body weight.

There are several uncertainties inherent in this guideline. The direct correlation between tissue residue and toxic effect was only done in one fish species, using two toxicant concentrations but in other respects, of high quality and long duration. Uncertainties also include those in the FWQG in the section above, plus those involved in the BCF/BAF estimation (point estimates of both the tissue and waterborne concentrations). There were few data for freshwater fish.

Federal Wildlife Dietary Guidelines

The Federal Wildlife Dietary Guidelines (FWiDGs) are intended to protect mammalian and avian consumers of aquatic biota. These are benchmarks for concentrations of toxic substances in aquatic biota (whole body, wet-weight) that are consumed by terrestrial and semi-aquatic wildlife. The FWiDGs may not be appropriate to extrapolate the impacts of PFOS to terrestrial consumers other than mammalian and avian species (e.g., reptiles).

FWiDGs for PFOS were developed using laboratory-based toxicity data and associated critical toxicity values (CTVs). The CTV of a study was the lowest treatment dose at which adverse effects were observed amongst organisms as a result of PFOS consumption. CTVs were divided by an uncertainty factor (UF) of 100 to produce a set of tolerable daily intake (TDI) values. The UF of 100 was chosen to account for extrapolation from laboratory to field conditions, and for extrapolation from the observed effects level to a no-effect level. Finally, reference concentrations were calculated for a number of species based on the minimum mammalian TDI (for mammals) and avian TDI (for birds), and the food intake to body weight ratio (FI:BW) specific to that species.

Mammalian: Nine studies were evaluated for four different species, cynomolgus monkeys (*Macaca fasicularis*), rabbits (*Oryctolagus cuniculus*), mice and rats. TDIs, calculated as the critical toxicity value divided by an uncertainty factor of 100, ranged from 1.1 to 112 µg/kg bw.d. The lowest TDI of 1.1 µg/kg bw.d reported for rats came from a two-year, chronic toxicity diet study (Covance Laboratories 2002). The mammalian FWiDG of 4.6 µg/kg food was calculated by dividing the minimum observed TDI of 1.1 µg/kg bw.d by the maximum mammalian FI:BW of 0.24 kg food/kg bw.d for American mink (CCME 1998).

Avian: Dietary PFOS toxicity to three avian species, mallard (*Anas platyrhynchos*), northern bobwhite (quail) (*Colinus virginianus*) and Japanese quail (*Coturnix coturnix japonica*) were evaluated. For developing the avian FWiDG the selected CTV is the LOAEL dose rate in northern bobwhite of 772 µg/kg bw.d that resulted in reduced chick survival post exposure. By applying an UF of 100, a TDI of 7.7 µg/kg bw.d is produced and an avian FWiDG of 8.2 µg/kg food is calculated by dividing that TDI by the maximum avian FI:BW of 0.94 kg food/kg bw.d for Wilson's storm-petrel (CCME 1998). Given the long duration of both the avian and mammalian studies, the uncertainties relate primarily to lack of knowledge of interspecies sensitivity given the paucity of wildlife species in the data set. Therefore an uncertainty factor of 100 was selected (CCME 1998) for both the avian and mammalian dietary guidelines.

Federal Tissue Quality Guideline for Bird Egg

Laboratory studies provided egg toxicity data for three avian species: northern bobwhite, mallard and white leghorn chicken. For studies performed using mallard and quail as test subjects, the contaminant was administered via maternal transfer from the diet; in contrast, chicken studies administered PFOS via injection into the air cell of the egg.

The maternal transfer studies established a NOAEL of 53 µg PFOS/mL egg yolk in mallard; a LOAEL could not be determined. In quail, based on number of survivors as a percentage of eggs set, a LOAEL of 62 µg/mL egg yolk was established; the NOAEL in the pilot study with quail was 33 µg/mL yolk (Newsted et al. 2005).

Studies where PFOS was injected into the air cell of freshly-laid chicken eggs with subsequent incubation found that egg pipping (initial cracking of the egg by the chick during hatching) was reduced to about 67% at 5 µg/g PFOS whole egg compared with controls or with eggs injected with 0.1 µg/g whole egg (O'Brien et al. 2009). Peden-Adams et al. (2009) found no mortality in chicken eggs injected with 1, 2.5 or 5 µg/g egg and no effects on growth. They did however find significant tissue-level effects at all concentrations on development (brain asymmetry, significant only at the lowest concentration, no dose-response) and immune function (no dose response). The ecological significance of these effects is not known. A third study using PFOS injection into chicken eggs (Molina et al. 2006) was considered unacceptable (see O'Brien et al. 2009).

A field study compared reproductive success in tree swallows from a contaminated urban lake versus a reference lake (Custer et al. 2012). The authors concluded that PFOS concentrations above 0.15 µg/g egg were detrimental to hatching success, however, this study could not be considered in guideline development because of large variability in hatch success between the two field seasons, large variations in egg PFOS concentrations within clutches and concurrent exposure to other perfluorinated substances Nevertheless, the study should be borne in mind when interpreting PFOS residues in bird eggs.

The egg tissue residue guideline was developed by dividing the LOAEL for quail of 62 µg/mL yolk by a safety factor of 10 to give 6.2 µg/mL. This was subsequently converted to whole egg concentrations for easier comparison with archived whole egg tissue. Most PFOS is contained in the yolk (Newsted et al. 2007; Gebbink and Letcher 2012). Using yolk: albumin ratio of 3:7 (Gebbink and Letcher 2012), and assuming egg density of about 1, the final guideline is 1.9 µg/g whole egg.

Overall, the tests used two wildlife species. More importantly, egg exposure was via maternal transfer, a route of administration which is more natural than direct injection. Nevertheless there are few species studied and little replication.

Federal Soil Quality Guidelines (FSQG)

Federal soil quality guidelines were derived to protect key ecological function for four different land uses: agricultural, residential/parkland, commercial and industrial following "*A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*" (CCME 2006).

Given the physical and chemical properties of PFOS, the FEQGs for soil and groundwater were derived considering direct soil contact, the protection of primary, secondary and tertiary consumers exposed to PFOS via soil and food ingestion, the protection of freshwater life, the protection of livestock watering and irrigation water and the protection of more sensitive use sites (e.g., agricultural) from adjacent sites exposed via off-site migration (e.g., via wind erosion) (EC 2015b). The nutrient and energy cycling check was not derived because of lack of data. Details on data acceptability and guideline calculations for soil and groundwater are available in EC (2015b).

Soil contact

Laboratory studies provided toxicity data for 8 plant species (alfalfa, flax, lettuce, onion, potato, ryegrass, soybean tomato), and 3 invertebrate species (earthworm, springtail and mite) (Table 5). A total of 32 acceptable EC_{25} and IC_{25} endpoints were used in a species sensitivity distribution in which the 25^{th} percentile ($ESSD_{25}$) was 22.1 mg/kg soil (Figure 2). The soil contact value for Agricultural and Residential/Parkland is the threshold effects concentration (TEC) which is the $ESSD_{25}$/uncertainty factor = 22.1/2 = 11 mg/kg. An uncertainty factor of 2 was applied because of uncertainties associated with lab to field extrapolation. The soil contact value for Commercial and Industrial land uses is the Effects Concentration Low which is equal to the $ESSD_{50}$ (50^{th} percentile of the species sensitivity distribution) = 61 mg/kg.

Table 5: EC_{25}, IC_{25} and LC_{20} Data used for Species Sensitivity Distribution used to Derive the Soil Contact value for Agricultural, Residential/Parkland and Commercial and Industrial Land Uses for PFOS.

Common name	Exposure Duration (days)	Endpoint	Effect	Concentration (mg PFOS/ kg soil)	Magnitude of Effect (%)	Reference
Lettuce	21	LOEC	Height	3.91	23% reduction in height	Brignole et al. 2003
Ryegrass	21	IC_{25}	Shoot weight	7.51	25	Brignole et al. 2003
Lettuce	21	IC_{25}	Shoot weight	8.92	25	Brignole et al. 2003
Tomato	21	IC_{25}	Shoot weight	11.7	25	Brignole et al. 2003
Earthworm	56	IC_{25}	Avg weight per juvenile	12	25	Stubberud 2006
Onion	21	IC_{25}	Shoot weight	12.9	25	Brignole et al. 2003
Soil mite	28	IC_{25}	Number of juveniles produced	13	25	EC 2015
Tomato	21	IC_{25}	Height	22.1	25	Brignole et al. 2003
Onion	21	IC_{25}	Height	29.1	25	Brignole et al. 2003
Soil mite	28	IC_{25}	Number of juveniles produced	33	25	EC 2015
Earthworm	56	LOEC	Total weight of juveniles	40		Stubberud 2006
Ryegrass	21	IC_{25}	Height	46.3	25	Brignole et al. 2003
Earthworm	56	IC_{25}	Number of juveniles	48	25	Stubberud 2006
Onion	21	EC_{25}	Emergence	50.8	25	Brignole et al. 2003
Alfalfa	21	IC_{25}	Shoot weight	53.3	25	Brignole et al. 2003
Springtail (soil inverteb	28	IC_{25}	Number of juveniles produced	61	25	EC 2015a
Tomato	21	LOEC	Survival of emerged seedlings	62.5	27% reduction in seedling survival	Brignole et al. 2003
Earthworm	28	IC_{25}	Number of cocoons	67	25	Stubberud 2006

Flax	21	IC_{25}	Shoot weight	81.6		Brignole et al. 2003
Flax	21	IC_{25}	Height	97.6	25	Brignole et al. 2003
Alfalfa	21	IC_{25}	Height	102	25	Brignole et al. 2003
Soybean	21	IC_{25}	Shoot weight	160	25	Brignole et al. 2003
Springtail (soil invertebr	28	IC_{25}	Number of juveniles produced	177	25	EC 2015a
Ryegrass	21	EC_{25}	Emergence	203	25	Brignole et al. 2003
Ryegrass	21	LOEC	Survival of emerged seedlings	250	34% reduction in seedling survival	Brignole et al. 2003
Alfalfa	21	LOEC	Survival of emerged seedlings	250	29% reduction in survival	Brignole et al. 2003
Lettuce	21	LOEC	Survival	250	23% reduction in seedling survival	Brignole et al. 2003
Earthworm	14	LOEC	Survival	256	20% reduced survival	Joung et al. 2010
Soybean	21	IC_{25}	Height	284	25	Brignole et al. 2003
Tomato	21	EC_{25}	Emergence	311	25	Brignole et al. 2003
Alfalfa	21	EC_{25}	Emergence	372	25	Brignole et al. 2003
Lettuce	21	EC_{25}	Emergence	393	25	Brignole et al. 2003

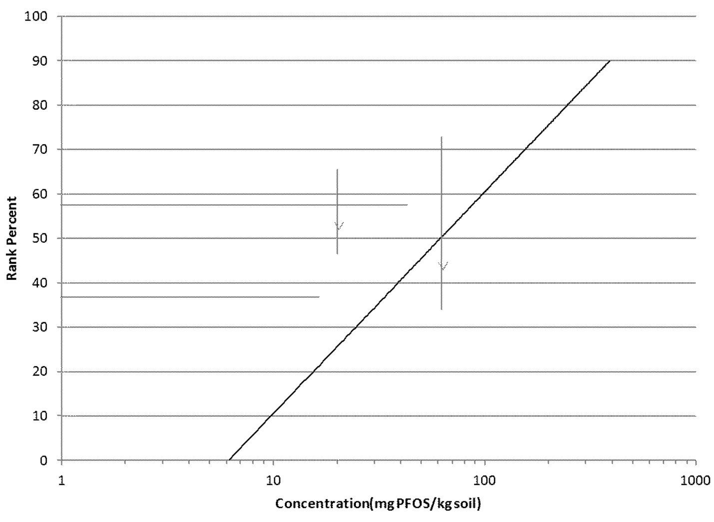

Figure 2. Estimated Species Sensitivity Distribution (ESSD) (Rank percent of EC_{25}/IC_{25} data) for PFOS for Terrestrial Plants and Invertebrates showing $ESSD_{25}$ and $ESSD_{50}$ used in guideline calculations.

Soil and Food Ingestion

Since PFOS is bioaccumulative, the soil FEQG for agricultural and residential/parkland land uses also considers exposure to primary, secondary and tertiary consumers in the food web. Table 6 provides the characteristics of the representative species used in the soil quality guideline calculations. The method used to calculate the soil quality guidelines to protect these consumers is found in CCME (2006).

***Primary-level consumers*:** Both herbivorous mammals (meadow vole) and birds (rock dove) were considered as indicator species (FCSAP 2012). For herbivorous mammals the lowest effects dose (ED_{1c}) of 0.1086 mg/kg bw/day (from Covance Laboratories Inc. 2002), was divided by an uncertainty factor of 2 according to methods described in the CCME protocol (2006) and based on the available data to obtain a daily threshold effects dose (DTED) of 0.0543 mg/kg bw/day. The FSQC to protect herbivorous mammals was 2.2 mg PFOS/ kg dry soil and 5.1 mg PFOS/kg dry soil to protect herbivorous birds. Therefore the lowest of the available $FSQG_{1C}$ is 2.2 mg PFOS/kg dry soil.

***Secondary consumers*:** The secondary food chain is more complex and involves up to three trophic levels. It can be represented by the following pathways:

a) Soil □ Prey (earthworms) □ Predator (Secondary consumer) (mammal-Common shrew or bird-American robin)
b) Soil □ Plant □ Prey (primary consumer) □ Predator (secondary consumer-deer mouse)

Table 6. Summary of Representative Species for Various Trophic Levels and Input Values for Calculation of Soil Quality Guidelines for PFOS.

Trophic Level	Feeding Guild	Representative Species	Diet[1]	Daily Threshold Effects Dose (mg/kg bw-day)	Body weight (kg)	Soil Ingestion Rate (kg dw/day)	Food Ingestion Rate (kg dw /day)	Bioconcentration Factor(s) (unitless) Soil □ plant Soil □ invertebrate Soil □ animal	FSQG to protect the receptor (mg PFOS/kg dry soil)[2]
Primary Consumer (1C)	Herbivorous mammal	Meadow vole	Plants	0.054	0.035	0.000041	0.00173	0.35 - -	2.2
	Herbivorous bird	Rock dove	Plants	0.386	0.31	0.0039	0.039	0.35 - -	5.1
Secondary Consumer (2C)	Insectivorous mammal	Common Shrew	Invertebrates (95%) Plants (2.5%) Small mammals (2.5%)	0.054	0.004	0.000032	0.0013	0.35 10.9 2.97	0.012
	Omnivorous mammal	Deer Mouse	Plants (50%) Invertebrates (50%)	0.054	0.02	0.000018	0.0009	0.35 10.9 -	0.17
	Omnivorous bird	American Robin	Plants (60%) Invertebrates (40%)	0.386	0.08	0.00059	0.015	0.35 10.9 -	0.33
Tertiary Consumer (3C)	Carnivorous mammal	Wolf	Mammals	0.054	80	0.0118	0.042	2.97	2.6
	Omnivorous mammal	Red Fox	Mammals and Birds (60%) Invertebrates (25%) Plants (15%)	0.054	3.8	0.0015	0.05	0.35 10.9 2.97	0.63

[1] Diet information provided in FCSAP (2012) and BC MOE (2001).
2 Bioavailability factor assumed to be equal to one in all cases.

The model developed to represent this food chain and to derive the $FSQG_{2C}$ is similar to the one used in deriving $FSQG_{1C}$. However, to account for biomagnification of PFOS from contaminated soil and food to the predator, the bioaccumulation factor from soil to prey (BAF_2) was used in addition to BCF_1. Three indicator species were considered: common shrew, deer mouse and American robin. Apportionment factors for foraging range and time spent on the site were both assumed to be one.

$FSQC_{2C}$ was 0.012 mg/kg dw soil (common shrew), 0.17 mg/kg dw soil (deer mouse) and 0.33 mg/kg dry soil (American robin). The lowest $FSQG_{2C}$ was therefore 0.012 mg PFOS/kg dry soil. This low value for $FSQG_{2C}$ is a function of: 1) the low body weight of shrew 2) the high food ingestion rate (FIR) of shrew relative to its body weight and 3) most (95%) of the shrew's diet being insects and invertebrates which have been shown to bioaccumulate PFOS to the greatest extent.

Tertiary consumer: The pathways for tertiary consumers considered predators consuming prey items which themselves have fed on contaminated plants. Given the available data from Müller et al. (2011) which provided a plant □ caribou □ wolf bioaccumulation factor data for PFOS, the following exposure pathways were considered for tertiary consumers:

a) soil □ plant □ caribou □ carnivorous mammal (wolf)
b) soil □ (plant + invertebrates + mammals + birds) □ omnivorous mammal (Red fox)

The bioaccumulation factor for tertiary consumers (BAF_{3C}) was derived from the $BCF_{\text{soil to plant}}$ x $BAF_{\text{plant to caribou}}$

$$BAF_{3C} = \frac{[\text{Herbivore}]}{[\text{Soil}]} = \frac{[\text{Plant}]}{[\text{Soil}]} \times \frac{[\text{Herbivore}]}{[\text{Plant}]}$$

Data were available for two caribou herds (Bathurst and Porcupine) (Müller et al. 2011). The geometric mean BAF for the two herds is $BAF_{\text{soil-herbivore}} = (3.185 \times 2.765)^{1/2} = 2.97$. The $FSQG_{3C}$ (carnivorous mammal, wolf) = 2.6 mg PFOS/kg dw soil and for omnivorous mammal (red fox) was 0.63 mg PFOS/kg dry soil. Therefore the lowest $FSQG_{3C}$ was 0.63 mg PFOS/kg dry soil.

Final SQG soil and food ingestion

As described in CCME (2006), the lowest of $FSQG_{1C}$, $FSQG_{2C}$ and $FSQG_{3C}$ was taken as the $FSQG_{\text{ingestion of soil and food}}$ or $FSQG_I$. In the case of PFOS, SQG_{2C} was the lowest and therefore $FSQG_I$ is 0.01 mg PFOS/kg dry soil.

Federal Soil Quality Guideline to Protect Livestock Watering

Contamination that migrates to groundwater may affect the water quality in dugouts, or water wells used for livestock watering or crop irrigation. These pathways apply only for the agricultural land use.

Determination of the federal soil quality guidelines for the protection of livestock watering ($FSQG_{LW}$) and irrigation ($FSQG_{IR}$) involves the application of the same groundwater model as for the $FSQG_{FL}$, however transport through the saturated zone is not considered. That is, it assumes that dugouts or wells could be installed within the contaminated area. The guidelines are calculated by setting the allowable receptor groundwater concentration in the model equal to the livestock water (for the $FSQG_{LW}$) and irrigation water (for the $FSQG_{IR}$) from the Canadian Water Quality Guidelines. If a livestock water guideline is not available, the livestock water threshold value can be developed using the following equation:

$$LWT = \frac{DTED \times BW}{WIR}$$

where:
LWT = calculated livestock water threshold value
DTED = DTED for livestock (mg PFOS/kg bw-day)
BW = livestock body weight (kg) = 550 kg for cattle (CCME 2000)
WIR = livestock water ingestion rate (L/day) = 100 L/day for cattle (CCME 2000)

Since a Canadian Water Quality Guideline for livestock water is not available, a DTED for livestock was calculated as:

$$LWT = \frac{0.1086 \text{ mg PFOS/ kg body weight-day} \times 550 \text{ kg}}{100 \text{ L/day}} = 0.597 \text{ mg/L}$$

Since the calculated livestock water threshold value is lower than the pure phase solubility of PFOS of 370 mg/L (see section 3 above), the calculation of the $FSQG_{LW}$ is required.

Using the same groundwater model as for the $FSQG_{FL}$, but where transport through the saturated zone not considered, with an input livestock water threshold of 0.597 mg/L, the resulting $FSQG_{LW}$ was 12 mg PFOS /kg for coarse soil and 9 mg PFOS/kg for fine soil. Since an irrigation water guideline was not available, the calculation of the $FSQG_{IR}$ was not required (CCME 2006).

Therefore the $FSQG_{LW}$ was 12 mg PFOS/kg soil for coarse soil and 9 mg PFOS/kg soil for fine soil.

Derivation of Federal Soil Quality Guidelines for the Protection of Off-site Migration

The soil contact pathway for commercial and industrial sites considers contact of ecological receptors with on-site soil only. However, wind and water erosion of soil can move contaminated soil from one site to another. CCME (2006) Appendix G describes a model to address this movement of soil from a commercial or industrial site to protect adjacent, more sensitive agricultural sites. Given the recognized imprecise nature of this model and the uncertainty associated with the input parameters, this pathway is considered a check mechanism only. It is recommended that professional judgement be used to determine whether the SQG should be modified by this pathway. Parameters considered included:

- Susceptibility of soil to erosion: a soil with 3% organic carbon and a sandy loam texture (73% sand, 19% silt and 8% clay) was considered representative of soil susceptible to erosion.
- Soil loss at the site due to wind and water erosion: CCME (2006) recognizes that soil loss due to water and wind erosion varies widely across Canada. The generic default soil loss was based on the average of wind and water erosion (measured in tonnes/ha) at Halifax, NS (wind 0.0, water 11.3) and Lethbridge, AB (wind 13.2, and water 3.3).
- Site conditions: The representative site had a slope of 1% and 650 kg/ha of vegetative surface cover, a bulk density of 1 t/m^3 and depth of depositional area of 0.14 cm.

Using the Universal Soil Loss Equation and the Wind Erosion Equation, the concentration in eroded soil from the commercial or industrial site that would raise the contaminant concentration in the receiving soil of an adjacent property equal to the agricultural guideline within a specified period of time was calculated. This concentration was applied as the federal soil quality guideline for off-site migration ($FSQG_{OM-E}$). At specific commercial or industrial sites, management actions may be needed to prevent or limit erosive losses of surface soils. Accommodation for such situations is provided in the guidance for the development of site-specific objectives (CCME 1996).

From CCME (2006)-Appendix G:

$SQG_{OM-E} = (14.3 \times FSQG_{Agr}) - (13.3 \times BSC)$
where:
$FSQG_{Agr}$ = the soil quality guideline protective of agricultural land uses (mg/kg) = 0.01 mg/kg
BSC = background soil concentration of the contaminant in the receiving soil (mg/kg)

Since PFOS is not naturally occurring, background soil concentrations (BSC) of PFOS in agricultural soils should be close to zero. Therefore the SQG_{OM-E} was 0.14 mg PFOS/kg soil.

Federal Soil Quality Guidelines ($FSQG_{FL}$) and Federal Groundwater Quality Guidelines ($FGWQG_{FL}$) for the Protection of Freshwater Life

Contaminants present in soil can migrate to groundwater given the characteristics of the contaminant together with certain hydrologic and hydrogeologic conditions. Where there are surface water bodies (streams, rivers, lakes, etc.) nearby, then aquatic life in these surface water bodies may be affected by contamination, particularly if there is a permeable aquifer connecting the contaminated soil with the surface water body.

The federal soil quality guideline for the protection of freshwater life ($FSQG_{FL}$) is a concentration in soil which is calculated to protect surface water aquatic life. The final federal groundwater quality guideline ($FGWQG_F$) is a concentration in groundwater which is protective of various pathway-specific guidelines (Table 3). For PFOS, the final groundwater guideline considered: i) the protection of soil-dependent organisms (such as plants) ($FGWQG_{GC}$), ii) the protection surface freshwater aquatic life where there is a minimum of 10 m lateral separation between the point of measurement (source) and the surface water body (receptor) ($FGWQG_{FL}$) and iii) the solubility of PFOS. Both the $FSQG_{FL}$ and $FGWQG_{FL}$ guidelines were developed by Franz (2012) by applying the fate and transport model described in CCME (2006 and 2015).

By setting the surface water quality guideline equal to the Federal Environmental Quality Guideline for freshwater aquatic life (FWQG) = 6.8 µg/L (0.007 mg/L) and using the models and default parameters in CCME (2006), the soil concentration ($FSQG_{FL}$) to prevent PFOS that might move through soil and groundwater from exceeding the surface water quality guideline was determined to be 0.21 mg/kg (for fine soil) and 0.14 mg/kg (for coarse soil) (Franz 2012). The federal groundwater quality guideline for the protection of freshwater life ($FGWQG_{FL}$) was calculated as 68 µg/L (0.068 mg/L) for both fine and coarse soil. The groundwater value to protect soil organisms (such as plants) from adverse effects via direct contact with groundwater was 2 mg/L. Therefore the final FGWQG, or $FGWQG_F$, is the lower of the two values or 0.068 mg/L (Table 3).

Assumptions, Uncertainties and Caveats for Groundwater Guidelines

The $FSQG_{FL}$, $FGWQG_{FL}$, and $FGWQG_{GC}$ values for soil and groundwater assume various hydrologic and hydrogeologic conditions as described in the CCME (2006 and 2015) model. Given the available data (Higgins and Luthy (2006, 2007), Higgins et al. (2007), Johnson et al. (2007), Chen et al.(2009, 2012), Ahrens et al. (2010, 2011), Enevoldsen and Juhler (2010), and Kwadijk et al. (2010)) the following model assumptions appear to be appropriate:

- sorption is the dominant attenuation mechanism for PFOS (i.e. no volatilization or biodegradation)
- sorption is described by the organic carbon to water partitioning coefficient (K_{oc}), and
- sorption is approximately linear over the range of aqueous PFOS concentrations relevant for deriving soil quality guidelines

Given the available data for PFOS, the arithmetic mean of log K_{oc} 3.32 L/kg was determined to be most appropriate for use in the CCME model (Franz 2012).

The sorption and desorption of PFOS may be greatly affected by organic carbon content, and the concentration of divalent calcium cation [Ca^{2+}]) in the aquatic environment (Higgins and Luthy (2006, 2007), Higgins et al.(2007), Johnson et al. (2007), Chen et al.(2009, 2012), and Kwadijk et al. (2010), Ahrens et al. (2010, 2011), Tang et al. (2010), Labadie and Chevreuil (2011), and Ferrey et al. (2012)). By affecting sorption, these factors also affect the bioavailability of PFOS to aquatic organisms, especially those more closely associated with sediments.

Since PFOS has been used in the formulation of fire-fighting foams, its release to the environment is often associated with hydrocarbon fuel fires and PFOS and oil or hydrocarbons are known to co-occur (Moody and Field (2000), Brooke et al. (2004), Chen et al. (2009)). This co-occurrence in soil also appears to have an effect on the partitioning of PFOS (Chen 2009). For example, the sorption of PFOS to oil was shown to be approximately an order of magnitude stronger than sorption to soil organic carbon, indicating oil is a potentially important sorption phase for PFOS particularly at the relatively low concentrations of PFOS in the ng/L to µg/L range (Chen et al. 2009). Additional research on this topic is warranted.

Given these considerations, where a site-specific groundwater or soil quality value may be required, the numerous site-specific hydrologic and hydro-geologic parameters would need to be considered, as outlined in CCME (2006 and 2015). These parameters include: organic carbon fraction in soil, water and air filled porosity, soil bulk density, solution chemistry, depth from soil surface to groundwater surface, hydraulic conductivity and hydraulic gradient in the saturated zone, infiltration rate, length and width of source parallel to groundwater flow, depth of the unconfined aquifer, and distance from source to receptor.

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List of Acronyms and Abbreviations

AF – Assessment Factor
AFFF- aqueous film forming foam
BAF – Bioaccumulation Factor: the ratio of the concentration of a chemical compound in an organism relative to the concentration in the exposure medium, based on uptake from the surrounding medium and food
BCF – Bioconcentration Factor: the ratio of the concentration of a chemical compound in an organism relative to the concentration of the compound in the exposure medium (e.g. soil or water)
BMF – Biomagnification Factor: a measure of bioaccumulation by which tissue concentrations of accumulated chemical compounds are determine relative to tissue concentrations in two or more trophic levels
CCME - Canadian Council of Ministers of Environment
CEPA - Canadian Environmental Protection Act
CMP - Chemicals Management Plan
CTV – Critical Toxicity Value
EC – Effect Concentration
ENEV – Estimated No Effect Value - usually established by dividing a critical toxicity value by an application factor that is derived on a substance-by-substance based as influenced by the quality and the quantity of the toxicity data
FTQG-BE – Federal Tissue Guideline - Bird Egg
FEQG - Federal Environmental Quality Guideline
FFTG – Federal Fish Tissue Guideline
FQWQG -Federal Groundwater Quality Guideline
$FGWQG_{Final}$ - Federal Groundwater Quality Guideline - Final
$FGWQG_{FL}$- Federal Groundwater Quality Guideline to Protect Freshwater Life
$FGWQG_{GC}$- Federal Groundwater Quality Guideline to protect organisms in direct contact with groundwater
$FGWQG_{IR}$ –Federal Groundwater Quality Guideline to protect irrigation water
$FGWQG_{LW}$ – Federal Groundwater Quality Guideline to protect livestock watering
$FGWQG_{M}$ – Federal Groundwater Quality Guideline- with management considerations
$FGWQG_{ML}$- Federal Groundwater Quality Guidelines to protect marine life FI: BW – Food Intake to Body Rate Ratio
FIR – food intake rate
$FSQG_{Agr}$ – Federal Soil Quality Guideline- agricultural land use
$FSQG_{Final}$- Federal Soil Quality Guideline- Final
$FSQG_{FL}$ - Federal Soil Quality Guideline to protect freshwater life
$FSQG_{I}$ – Federal Soil Quality Guideline for soil and food ingestion and is the lowest of the soil quality guidelines calculated to protect primary, secondary and tertiary consumers
$FSQG_{LW}$ – Federal Soil Quality Guideline for the protection of livestock watering
$FSQG_{OM-E}$- Federal Soil Quality Guideline for the protection of more sensitive land uses (e.g., agricultural) from the off-site movement of soil from commercial or industrial sites
$FSQG_{SC}$- Federal Soil Quality Guideline to protect organisms (e.g. earthworms, plants) in direct contact with soil
$FSQG_{1C}$- Federal Soil Quality Guideline for soil and food ingestion by primary consumers (e.g. herbivorous mammal (vole), herbivorous birds (rock dove)
$FSQGC_{2C}$ - Federal Soil Quality Guideline for soil and food ingestion by secondary consumers (e.g. insectivorous mammal (shrew), omnivorous mammal (deer mouse), omnivorous bird (robin)
$FSQG_{3C}$ - Federal Soil Quality Guideline for soil and food ingestion by tertiary consumers (e.g., carnivorous mammal (wolf), omnivorous mammal (fox))
FWiDG – Federal Wildlife Diet Guideline
FWQG - Federal Water Quality Guidelines
IC - Inhibition concentration

K_d – Distribution Coefficient
K_{ow} – Octanol Water Partition Coefficient
LOEC – Lowest Observed Effect Concentration
LOAEL – Lowest Observed Adverse Effect Level
MATC - Maximum Acceptable Toxicant Concentration
N-EtFOSE alcohol - 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol
N-MeFOSE alcohol – 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol
NOAEL – No Observed Adverse Effect Level
NOEC- No Observed Effect Level
OECD – Organization for Economic Co-operation and Development
PFCs – perfluorinated compounds
PFOS – Perfluorooctane Sulfonate
SAR – Screening Assessment Report
SSD – Species Sensitivity Distribution
TDI – Tolerable Daily Intake